KFKI-72-72

Á. I. Kiss
J. Szőke

QUANTUMSPECTROSCOPY

No 7. Pi-electron SCF-MO calculations for disubstituted benzene derivatives containing two acceptor groups

Part two: Numerical results of calculations

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Pi-ELECTRON SCF-MO CALCULATIONS FOR DISUBSTITUTED BENZENE DERIVATIVES CONTAINING TWO ACCEPTOR GROUPS

Part Two:

Numerical Results of Calculations

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ABSTRACT

The π-electronic structures and spectra of disubstituted benzene derivatives containing carbonyl, carboxy, and nitro groups have been calculated by the Pariser-Parr-Pople method. For all disubstituted derivatives the same starting parameters, determined from the spectra of the monosubstituted compounds, were used. The calculations give good results for the singlet transition energies as well as for the ground state charge densities and bond orders.

РЕЗЮМЕ

Методом Паризера-Парра-Папла были вычислены π-электронные структуры и спектры двузамещенных производных бензола, содержащих карбонильную, карбоксильную и нитро группы. Для расчетов каждого двузамещенного производного были использованы одинаковые исходные параметры, определенные из спектров однозамещенных производных. Хорошие результаты были найдены для энергии синглетных переходов, а также для распределения плотности зарядов и порядков связи в основном состоянии.

KIVONAT

Karbonil-, karboxil- és nitro-csoportot tartalmazó diszubsztituált benzolszármazékok π-elektronszerkezetét és szinképét számitottuk Pariser--Parr-Pople módszerrel. Minden diszubsztituált származékot azonos, a monoszubsztituált származékok szinképe alapján meghatározott kiindulási értékekkel számitottunk. A számitások jó eredménnyel adták a szinglet átmenetek energiáját, valamint az alapállapotu töltéssürüség- és kötésrend-értékeket.

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Table 1.

1. CALCULATED AND EXPERIMENTAL SPECTRAL DATA

Compound	Calculated			Experimental[a/]			Ref.
	E(eV)	f	α^{o}	E(eV)	$\log\varepsilon$	f	
BENZALDEHYDE	4.526	0.026	111.1	4.460	2.97	0.022	1
	5.166	0.575	191.6	5.155	4.03	0.257	
	6.244	0.398	279.7				
	6.547	0.648	195.1				
BENZOIC ACID	4.643	0.016	119.2	4.525	3.02	0.025	1
	5.380	0.509	11.8	5.367	4.20	0.384	
	6.159	0.010	44.3				
	6.489	0.720	95.4				
NITROBENZENE	4.564	0.029	90.0	4.320	3.08	0.029	
	5.067	0.418	0.0	4.949	3.97	0.224	1
	5.899	0.018	270.0				
	6.080	0.289	90.0	5.961	3.99	0.235	
BENZENE-O-DIALDEHYDE	4.253	0.060	236.5	4.174	3.36	0.055	2
	4.726	0.324	142.6	4.862	3.95	0.214	
	5.650	1.156	221.4				
	5.945	0.268	302.0				
	6.826	0.015	205.2				
	6.881	0.009	355.9				
BENZENE-M-DIALDEHYDE	4.319	0.017	161.1	4.275	3.18	0.036	3
	5.095	0.257	248.9	5.166	4.11	0.309	
	5.345	1.149	156.3	5.510	4.15	0.339	
	5.787	0.366	40.0				
	6.785	0.113	353.9				
	6.995	0.296	250.0				
BENZENE-P-DIALDEHYDE	4.230	0.060	297.0				
	4.741	0.920	14.2				
	6.090	0.000	70.5				
	6.225	0.478	277.1				
	6.290	0.000	269.6				
	6.588	0.840	192.9				
O-FORMYLBENZOIC ACID	4.353	0.040	220.7	4.492	2.93	0.020	4
	4.841	0.272	309.9	5.535	3.90	0.192	
	5.700	0.060	244.6				
	5.742	1.118	214.6				
	6.206	0.633	104.2				
	6.648	0.007	59.1				
	7.001	0.032	326.3				
	7.261	0.126	39.6				

/Table 1. Continued/

Compound	Calculated			Experimental [a/]			Ref.
	E(eV)	f	α^{o}	E(eV)	logε	f	
M-FORMYLBENZOIC ACID	4.374	0.019	182.1				
	5.154	0.333	285.7				
	5.504	0.986	167.1				
	5.923	0.335	43.7				
	6.100	0.119	329.7				
	6.408	0.184	280.2				
	6.956	0.239	297.3				
	7.047	0.369	237.5				
P-FORMYLBENZOIC ACID	4.320	0.052	300.4	4.305	3.29	0.047	4
	4.819	0.858	14.1	4.979	4.24	0.420	
	5.788	0.033	116.1				
	6.189	0.360	273.2				
	6.289	0.039	271.7				
	6.570	0.528	174.4				
	6.649	0.459	213.7				
	7.031	0.091	284.4				
O-NITROBENZALDEHYDE	4.301	0.084	59.4	4.217	3.22	0.040	1
	4.772	0.309	142.4				
	5.450	0.094	183.2	5.019	3.85	0.170	
	5.618	0.755	226.3				
	5.842	0.141	313.0				
	6.496	0.121	81.8				
	6.686	0.048	328.4				
	6.775	0.530	278.0				
M-NITROBENZALDEHYDE	4.399	0.011	130.3	4.290	3.02	0.025	1
	5.062	0.178	206.5	5.081	4.00	0.240	
	5.351	0.987	147.2	5.510	4.01	0.245	
	5.662	0.155	201.8				
	5.942	0.310	87.4				
	6.270	0.045	274.8				
	6.656	0.247	225.2				
	6.946	0.212	302.5				
P-NITROBENZALDEHYDE	4.286	0.056	102.5	4.174	3.37	0.056	1
	4.796	0.753	187.1	4.805	3.97	0.224	
	5.619	0.082	90.5				
	5.959	0.076	250.0				
	5.971	0.010	166.5				
	6.369	0.309	286.1				
	6.574	0.751	191.4				

/Table 1. Continued/

Compound	Calculated			Experimental [a/]			Ref.
	E(eV)	f	α^{o}	E(eV)	logε	f	
BENZENE-O-DICARBOXYLIC ACID	4.393	0.046	257.8	4.492	3.16	0.035	5
	4.871	0.198	140.1	5.414	3.96	0.219	
	4.965	0.075	353.8				
	5.703	0.616	227.7				
	5.903	0.064	214.7				
	6.275	0.577	251.9				
	6.340	0.629	161.2				
	6.956	0.074	105.8				
BENZENE-M-DICARBOXYLIC ACID	4.454	0.011	165.2	4.396	2.98	0.023	5
	5.251	0.206	248.9	5.390	4.08	0.288	
	5.570	1.048	339.6	5.932	4.59	0.933	
	5.975	0.110	192.5				
	6.181	0.236	294.7				
	6.194	0.406	41.3				
	6.485	0.019	199.4				
	6.641	0.202	256.9				
BENZENE-P-DICARBOXYLIC ACID	4.417	0.043	306.3	4.335	3.23	0.041	6
	4.939	0.813	193.9	5.123	4.21	0.389	
	5.819	0.000	120.0				
	5.975	0.038	281.7				
	6.319	0.665	92.5				
	6.457	0.000	120.0				
	6.619	0.885	185.6				
	6.843	0.000	120.0				
O-NITROBENZOIC ACID	4.255	0.090	83.7	4.275	3.10	0.030	1
	4.604	0.143	155.6				
	4.750	0.152	170.0	5.275	3.82	0.158	
	5.570	0.346	229.4				
	5.702	0.153	245.7				
	5.845	0.210	304.8				
	6.221	0.307	191.6				
	6.678	0.267	287.1				
M-NITROBENZOIC ACID	4.431	0.011	101.9	4.189	2.88	0.018	1
	5.031	0.251	10.2	5.040	3.89	0.186	
	5.468	0.753	145.5	5.661	4.43	0.646	
	5.731	0.223	175.3				
	5.927	0.057	109.9				
	6.050	0.227	263.3				
	6.134	0.127	253.5				
	6.513	0.010	276.7				

/Table 1. Continued/

Compound	Calculated			Experimental[a/]			Ref.
	E eV	f	α^{o}	E eV	logε	f	
P-NITROBENZOIC ACID	4.370	0.047	285.7	4.275	3.88	0.058	1
	4.819	0.670	7.3	4.900	4.15	0.339	
	5.688	0.094	284.1				
	5.713	0.032	266.2				
	5.983	0.160	80.6				
	6.148	0.008	18.1				
	6.513	0.367	315.5				
	6.634	0.750	200.9				
O-DINITROBENZENE	4.452	0.070	30.0	4.428	3.14	0.033	1
	4.755	0.020	300.0				
	4.965	0.000	210.1				
	5.052	0.197	300.0	5.166	3.90	0.191	
	5.697	0.645	210.0	5.848	4.19	0.372	
	5.880	0.253	120.0				
	6.035	0.222	120.0				
	6.154	0.164	210.0				
M-DINITROBENZENE	4.495	0.023	150.0	4.350	2.98	0.023	1
	5.174	0.122	240.0				
	5.348	0.725	150.0	5.462	4.33	0.513	
	5.667	0.003	240.0				
	5.724	0.132	330.0				
	5.870	0.301	60.0				
	6.053	0.042	150.0				
	6.081	0.207	240.0				
P-DINITROBENZENE	4.344	0.057	270.0	4.217	3.28	0.046	1
	4.945	0.659	0.0	4.862	4.18	0.363	
	5.502	0.173	90.0				
	5.504	0.000	270.0				
	5.942	0.000	120.0				
	5.997	0.000	120.0				
	6.279	0.157	90.0				
	6.529	0.616	0.0				

NOTE:

[a/] The experimental data refer to cyclohexane solution, with the following exceptions: benzene-m-dialdehyde is measured in methanol, benzene-o- and m-dicarboxylic acid in 0.1 N HCl, and benzene-p-dicarboxylic acid in dioxane.

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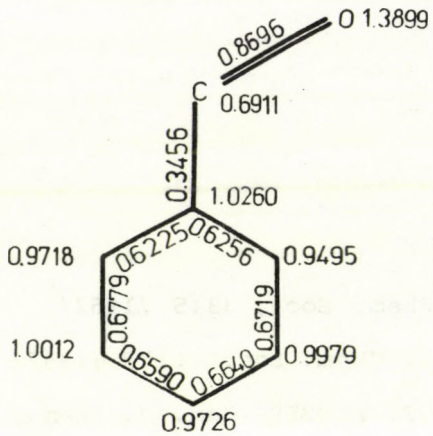
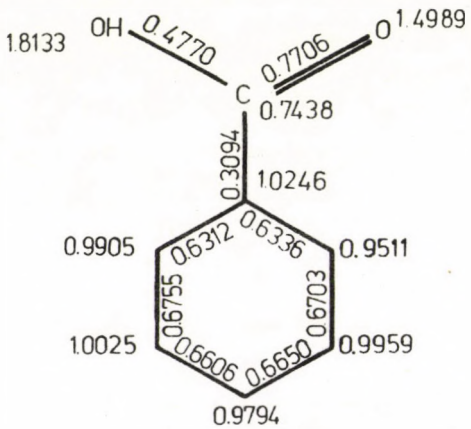
3. CHARGE DENSITIES AND BOND ORDERS

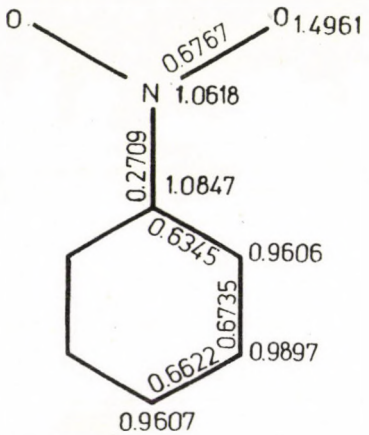
3.1 Benzaldehyde



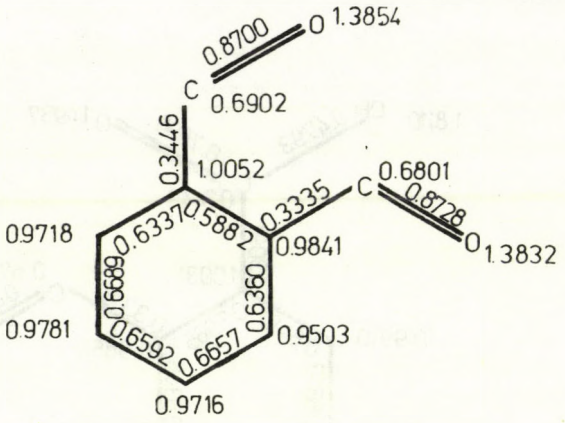
3.2 Benzoic acid

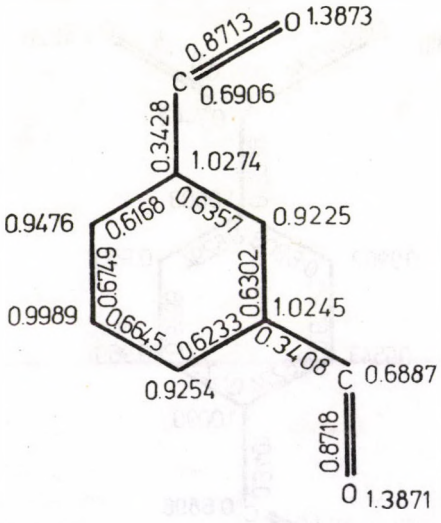


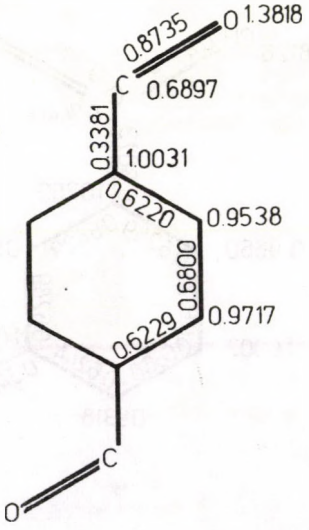
3.3 Nitrobenzene



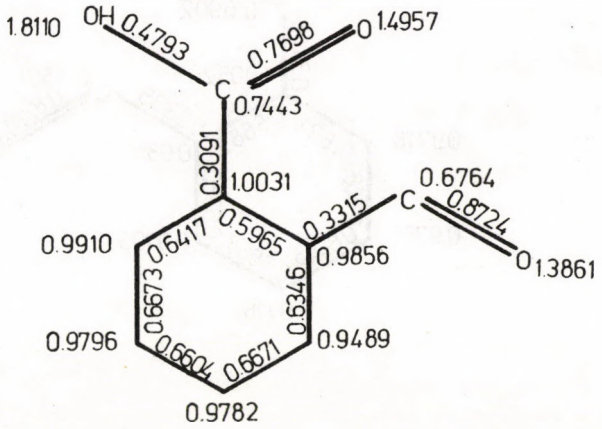
3.4 Benzene-dialdehydes

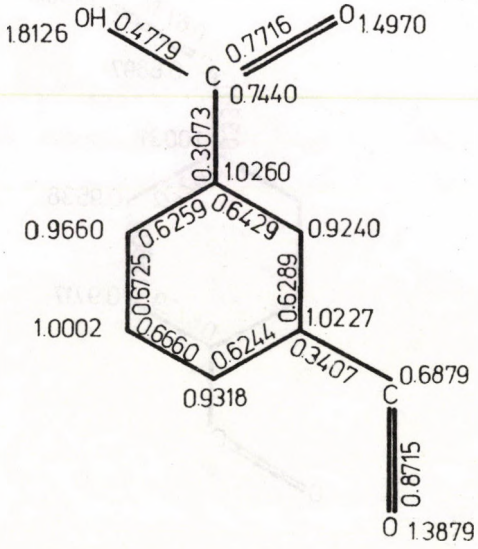


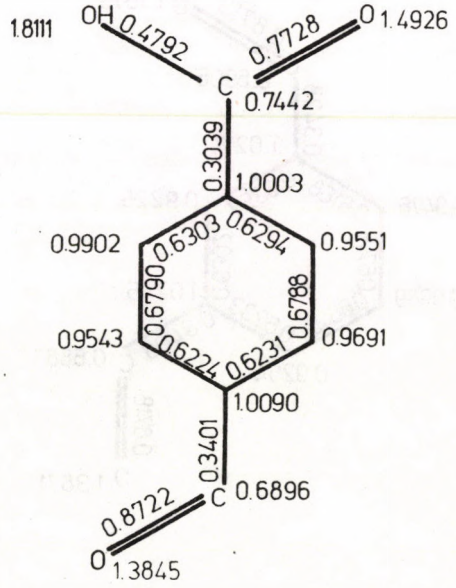




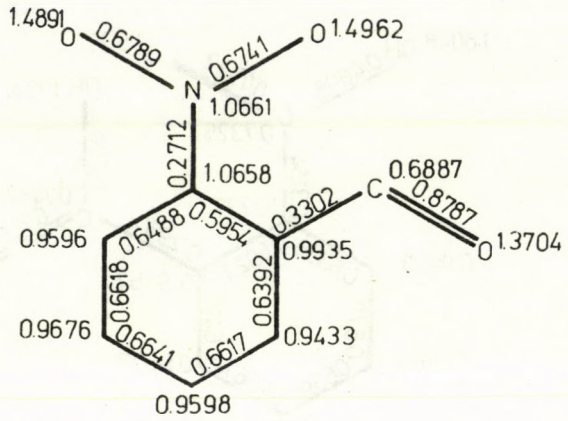
3.5 Formylbenzoic acids

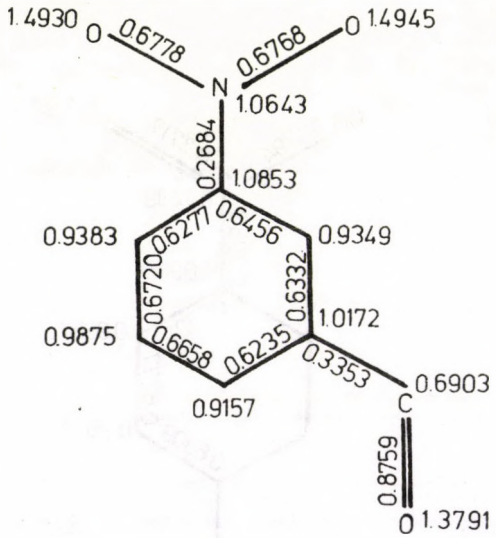


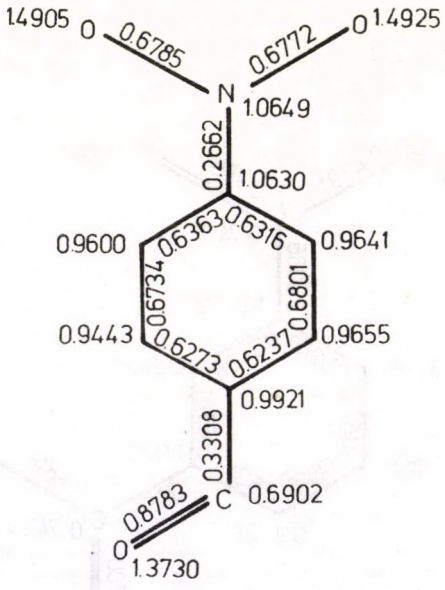




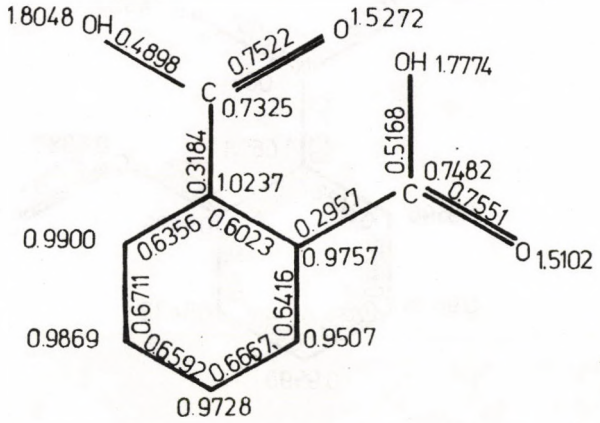
3.6 Nitrobenzaldehydes

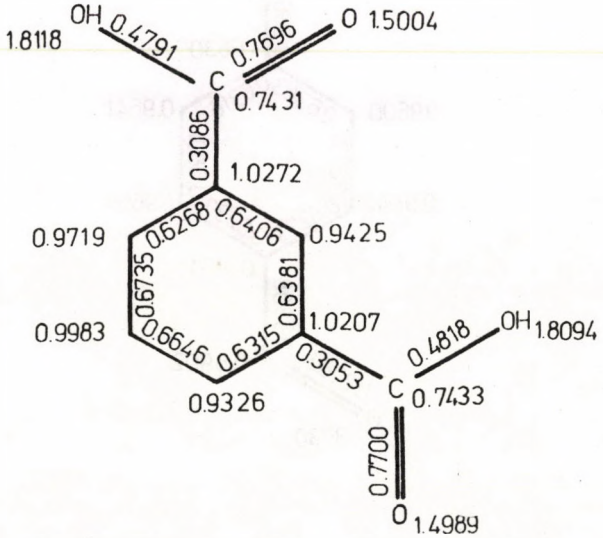


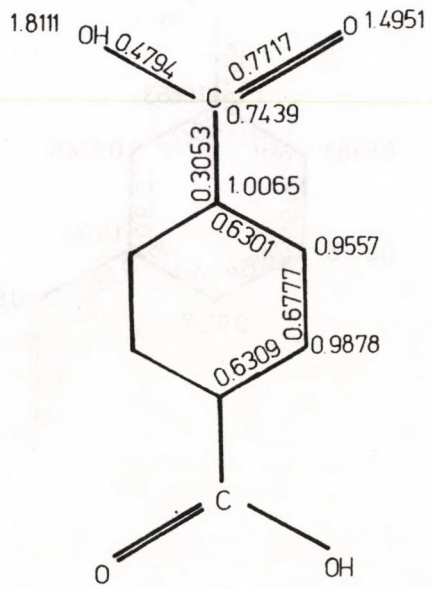




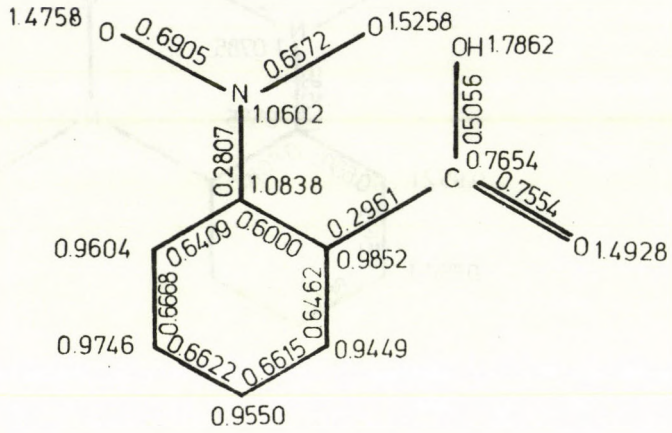
3.7 Benzene-dicarboxylic

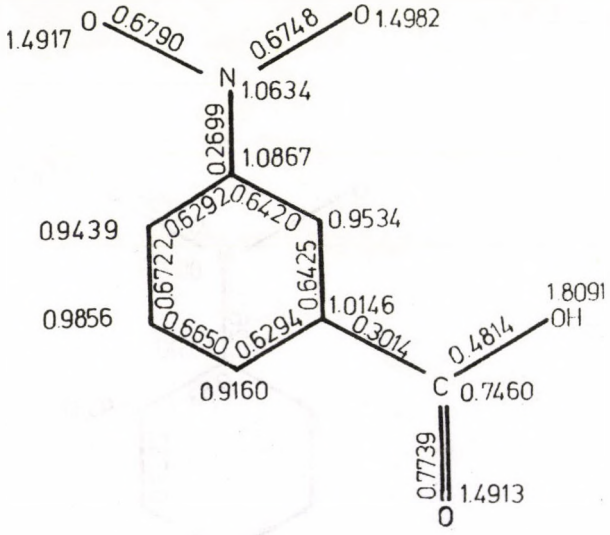


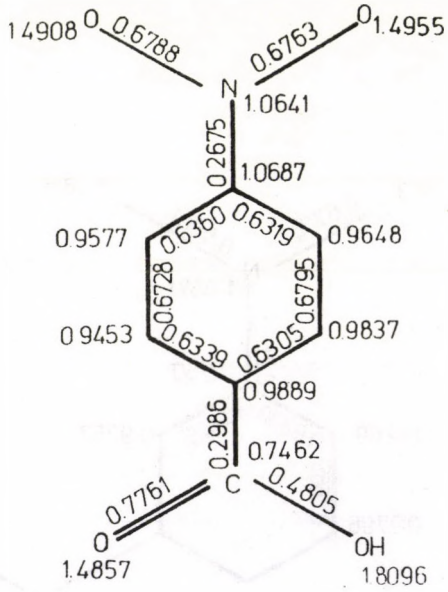




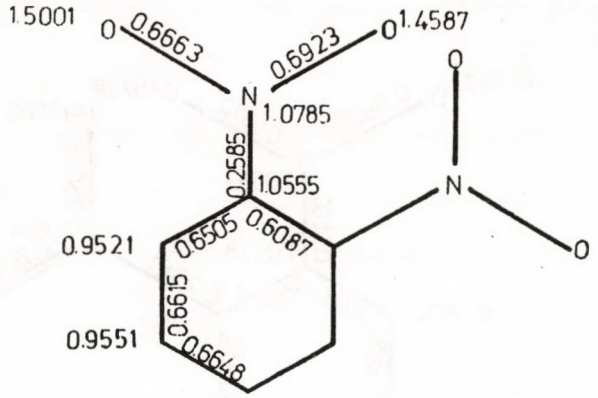
3.8 Nitrobenzoic acids

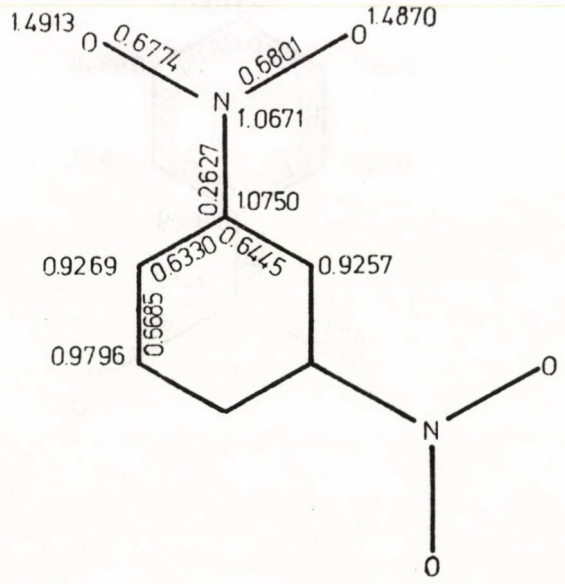


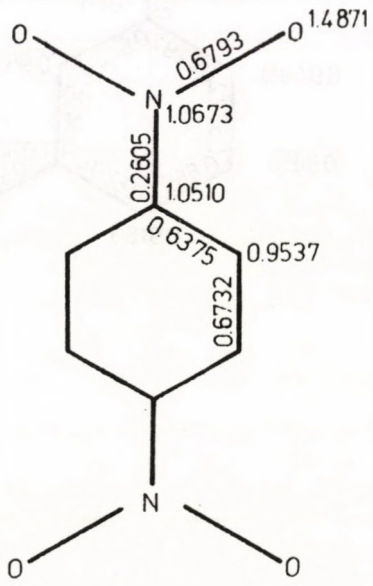




3.9 Dinitrobenzenes







4. CORRELATIONS BETWEEN THE CALCULATED AND EXPERIMENTAL TRANSITION ENERGIES

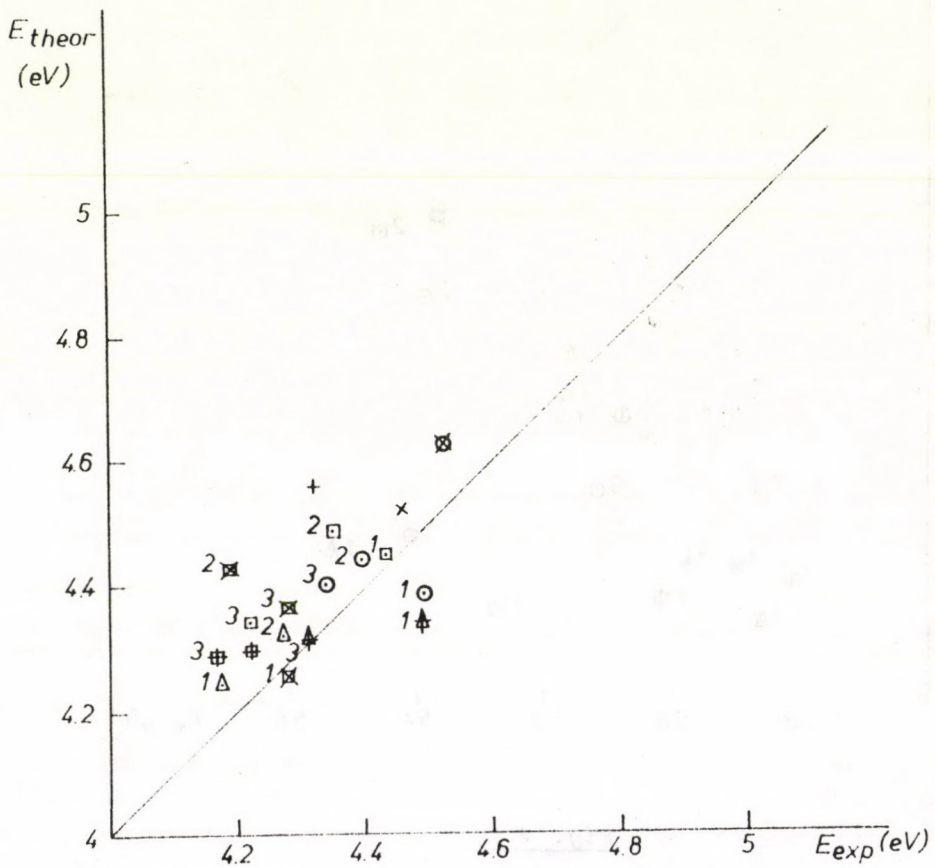


Fig. 4.1

Correlation between the calculated and experimental energy of the α band

× *CHO*; ⊠ *COOH*; + NO_2; ⧋ *CHO, CHO*; ⧓ *CHO, COOH*; ⧗ *CHO,* NO_2; ⊙ *COOH, COOH*; ⊠ *COOH,* NO_2; ⊡ NO_2, NO_2

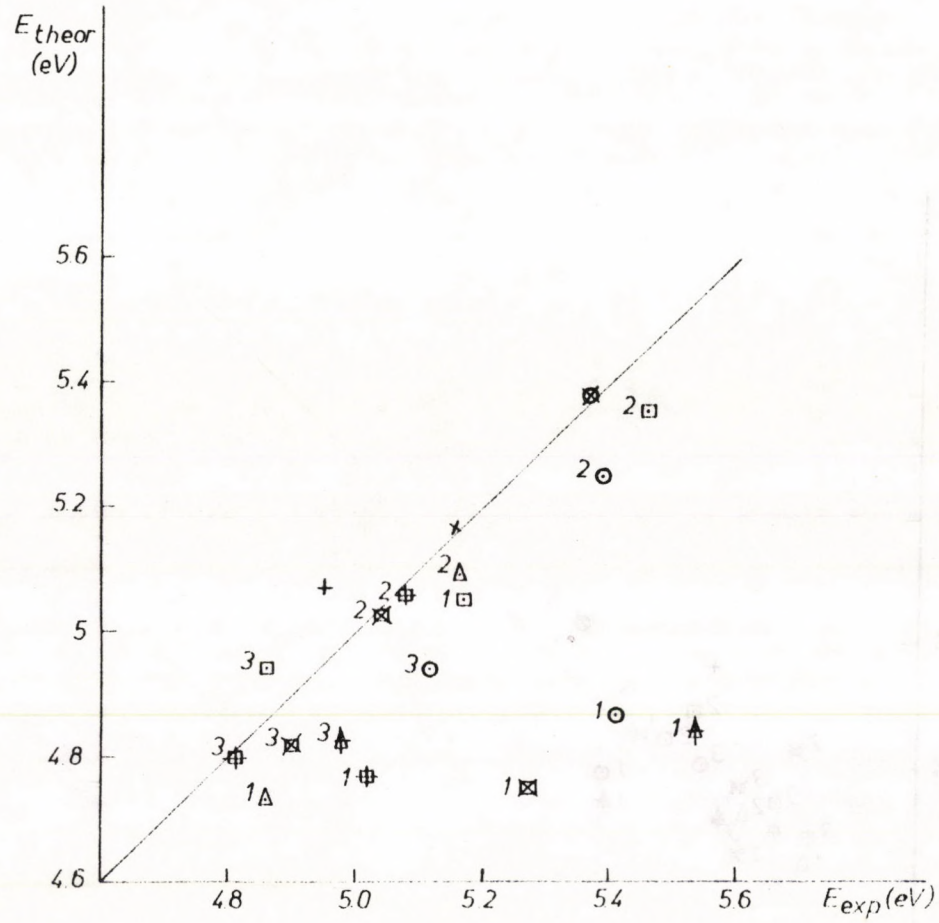
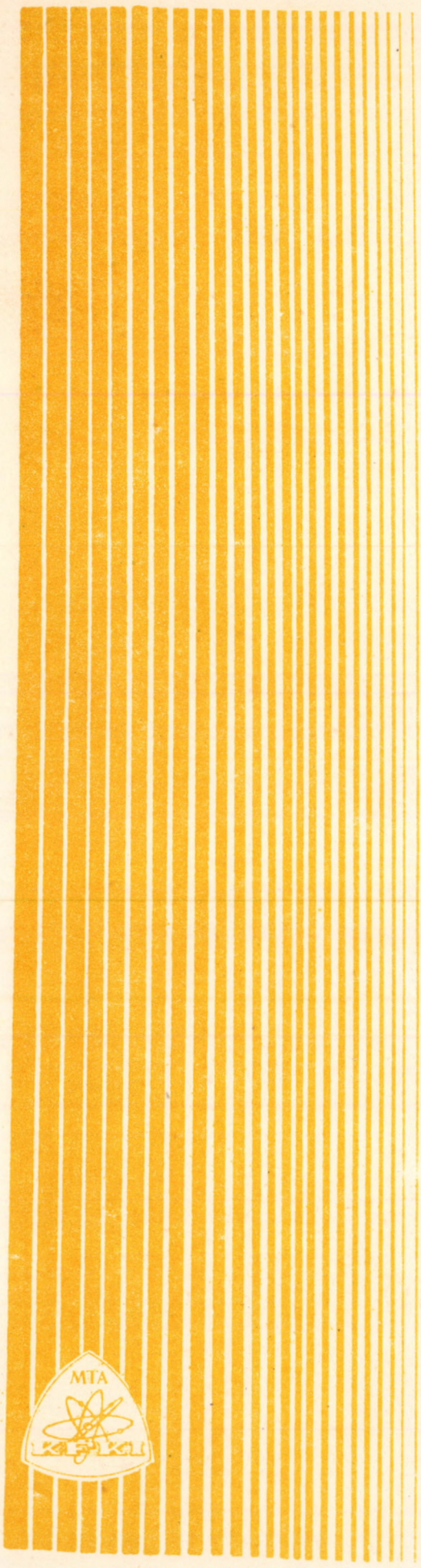


Fig. 4.2

Correlation between the calculated and experimental energy of the p band

For notation see caption of Fig. 1.



Kiadja a Központi Fizikai Kutató Intézet
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Budapest, 1973. január hó